

ELECTROCHEMICAL PERFORMANCE TESTING

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OVERVIEW

Timeline

- Facility established: 1976
- End: Open this is an on-going activity to test/validate/document battery technology as technologies change and mature

Budget

- DOE Funding FY18: \$1.2 M (expected); \$500K (received)
- FY17: \$1.8 M
- FY16: \$1.8 M

Barriers

- Performance (power and energy densities)
- Cycle Life (1,000-450,000 cycles depending on application)
- Calendar Life (15 y)
- Low-temperature performance
- Fast Charging

Collaborations

- US battery developers
- Idaho National Laboratory, Sandia National Laboratories, National Renewable Energy Laboratory
- CATARC (China)



RELEVANCE

Objective

- To provide DOE and the USABC an independent assessment of contract deliverables and to benchmark battery technology not developed under DOE/USABC funding
- To provide DOE and the USABC a validation of test methods/protocols
- To develop methods to project battery life and to use these methods on test data
- To investigate the effect of fast charge on battery life

Approach

- Apply standard, USABC testing methods in a systematic way to characterize battery-development contract and benchmarking deliverables
- Characterize cells, modules and packs in terms of:
 - Initial performance
 - Low temperature performance/Cold cranking
 - Cycle life
 - Calendar life
- Compare test results to DOE/USABC goals
- Adapt the test facility hardware and software
 - to accommodate programmatic need and needs of a given technology and/or deliverable



PROGRAM MILESTONES

Milestone	Date	Status
Submit quarterly reports to DOE and USABC	12/31/17	Complete
Submit quarterly reports to DOE and USABC	3/31/18	Complete
Submit quarterly reports to DOE and USABC	6/30/18	On track
Submit quarterly reports to DOE and USABC	9/30/18	



TECHNICAL ACCOMPLISHMENTS: PROGRESS AND RESULTS – TESTING CONTRACT DELIVERABLES

- Test deliverables are mostly cell-oriented and include developments in
 - Lithium-ion battery chemistry (graphite anodes)
 - Silicon anodes
 - Battery recycling
 - Ultra capacitors

- Lithium metal anodes
- Separators
- Advanced cell chemistries (beyond Li-ion)
- Deliverables are characterized in terms of initial capacity, resistance, energy and power. They are then evaluated in terms of cycle and calendar life for the given application
- Results are used to show progress toward meeting DOE/USABC initial commercialization goals



PROGRESS AND RESULTS – TESTING CONTRACT DELIVERABLES

Developer	Sponsor	Level	Quantity	Rated Capacity, Ah	Application	Status
Maxwell	USABC	Cell	6	0.357	12-V S/S	complete
	USABC	Module	15	40	12-V S/S	on-going
	USABC	Cell	20	0.357	12-V S/S	on-going
	USABC	Cell	6	0.79	EV	complete
	USABC	Cell	18	6	EV	on-going
24-M	USABC	Cell	18	10	EV	expected
	DOE FOA	Cell	10	4.3	EV	complete
	DOE FOA	Cell	4	105	EV	complete
Navitas	DOE FOA	Cell	24	14	EV	on-going
INAVILAS	DOE FOA	Cell	13	2/4	EV	complete
Microcure	DOE FOA	Cell	6	2.2	EV	complete
LGChem	DOE	Cell	10	25.9	PHEV-40	complete
XALT	DOE FOA	Cell	24	95	EV	on-going
WPI	USABC	Cell	40	1	Recycling/PHEV-20	on-going
	USABC	Cell	30	11	Recycling/PHEV-19	on-going
	USABC	Cell	40	1	Recycling/EV	expected
	USABC	Cell	30	10	Recycling/EV	expected
	USABC	Half cell	9	0.00236	EV	complete
	USABC	Cell	8	0.00156	EV	complete
SiNode	USABC	Cell	20	1	EV	on-going
	USABC	Cell	9	0.55	EV	on-going
	USABC	Cell	20	10	EV	expected
	USABC	Cell	18	2	Recycling/PHEV-20	expected
Farasis	USABC	Cell	24	2	Recycling/PHEV-20	expected
	USABC	Cell	30	25	Recycling/PHEV-20	expected
Daikin	DOE	Cell	9	1	EV/PHEV	complete
Celgard	USABC	Cell	6	1.1	EV	complete
ANL -CAMP	DOE	Half cell	75	0.0034	XFC-GITT	on-going
	DOE	Cell	15	19	XFC/Temp Study	on-going
	DOE	Cell	15	TBD	XFC/Temp Study	expected
A123	DOE	Cell	39	2.5	US-China	complete

- Test deliverables come from many developers
- Deliverables are tested for various automotive applications



PROGRESS AND RESULTS – COLLABORATIVE US/CHINA FAST CHARGE COMPARISON

- With further vehicle electrification, customers would desire battery charging to take the same amount of time as refueling an ICE does at a service station. This does not have to be a full charge
- There are parallel testing efforts, such as those in the US and China, which may be better leveraged through international collaboration
- The Chinese Fast Charge Test consists of full cycles from empty to full including CV to manufacturer recommended taper at 25°C.
- For comparison, complete fast charge cycles from empty to full were applied to an additional group of cells at 30°C, using USABC metrics for RPTs.
- Further work compared these degradations to those defined in the USABC rev 2 and rev 3 EV manuals. Rather than full cycles, the USABC EV manual definitions are:
 - Fast charge from 60% DOD to 20% DOD at increasing rates (rev 2)
 - Fast charge from 80% DOD at 3.2C for 15 minutes. CV as necessary (rev 3)
- A test plan based on an EV application was agreed upon



CONDUCT SIDE-BY-SIDE EXPERIMENTS

 Commercially-available batteries based on LiFePO₄ and carbon were procured. The batteries were distributed to ANL and CATARC (China)

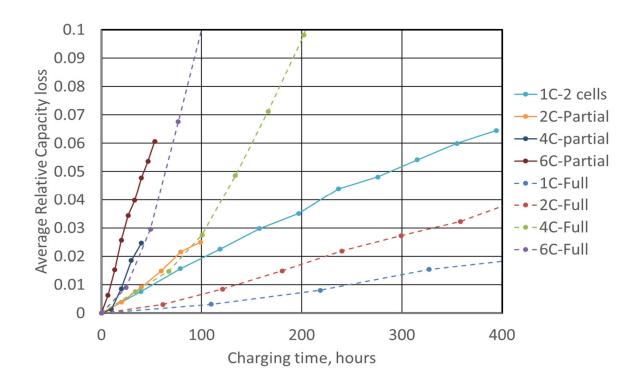
Test Name	Protocol	Charge Rates	Temperature (°C)	RPT capacity rate	Power pulse	Pulse DOD
Fast Charge I - US	Full cycles from empty to full	1, 2, 4 and 6-C	30	C/3	20A, 30s	Every 10%
Fast Charge II - US	Partial cycles from 60 to 20% DOD	1, 2, 4 and 6-C	30	C/3	20A, 30s	Every 10%
Fast Charge III - US	Partial cycles from 80% DOD for 15	3.2C	30	C/3	20A, 30s	Every 10%
Fast Charge - China	Full cycles from empty to full	1, 2, 4 and 6-C	25	C/1	45A, 5s	50%

- All tests used full capacity cycles at 1-C, 2-C, 4-C and 6-C charging rates
- Discharge was always at 1-C rate for aging of Fast Charge I
- Discharge was C/3 rate for Fast Charge II and III
- Thirty minute rest periods between steps
- Three cells per condition
- USABC Reference Performance Test consisted of 1 C/3 capacity cycle and 30 second peak power pulse test at 10% DOD increments. The cells are characterized using these performance tests every 100 cycles at 30°C
- China Reference Performance Test consists of 1 C/1 capacity cycle and 5 second discharge pulse after discharging at C/1 for 1800 seconds. The performance of the cells were characterized using these performance tests every 100 cycles at 25°C
- Some fast-charge data from China was received; however, the comparison between the data sets is incomplete



CAPACITY FADE OVER CYCLE LIFE – FAST CHARGE I VS. II

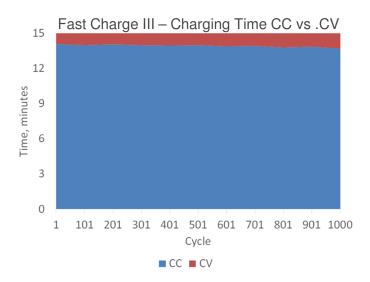
- Fast Charge II is fading at a slightly higher rate vs. charge time
- This may be related to the added capacity throughput in this profile



FAST CHARGE II VS. III CHARGE TIME

- No CV during Fast Charge II (yet)
- Charge times therefore identical for each rate across life
- Minimal shift in time from CC to CV during Fast Charge III

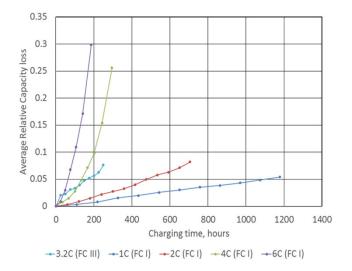
Fast Charge II Charging Time, seconds				
Cycle	1C rate	2C rate	4C rate	6C rate
1	1422	714	359	240
101	1420	714	359	240
201	1419	714	359	239
301	1419	714	359	240
401	1419	714	359	239
501	1418	714		239
601	1417			239
701	1422			239
801	1421			239
901	1421			
1000	1422			

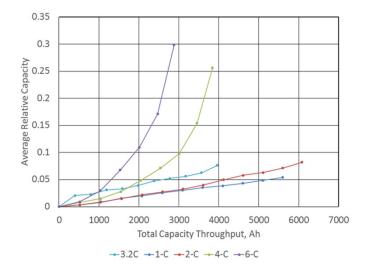




FAST CHARGE III - CAPACITY

- Charge at 3.2C for 15min from 80% DOD, then CV as necessary
- Compared to Fast Charge I, initial fade greater than 4C and 6C rates
- Similar observations whether over charge-time or capacity throughput

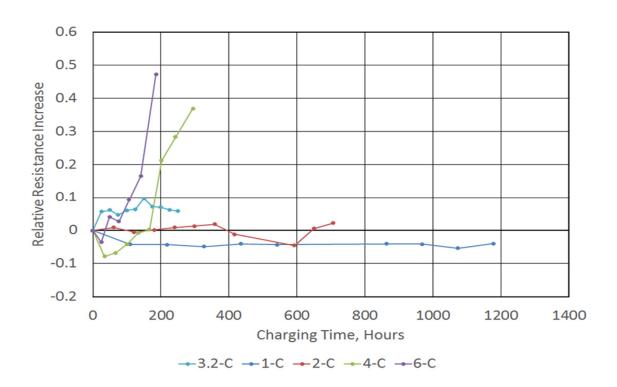






FAST CHARGE III - RESISTANCE INCREASE

- 3.2C rate cells did not initial drop in DC resistance
- Degradation rate at 3.2C rate found between 2C and 4C fade rates after 700 cycles



POST-TEST ANALYSIS OF FAST-CHARGED CELLS

- After the fast-charge experiments, selected cells will be torn down and their components characterized to elucidate failure modes
- Lithium plating
 - Scanning Electron Microscopy Utility will depend on amount and morphology of lithium plated; EDS cannot detect Li directly
 - XPS In principle, XPS can detect lithium. However, in practice it may be difficult due to:
 - Quantity of lithium
 - Difficult to resolve Li from Li₂O
 - Reactivity of nascent Li with electrolyte, producing an SEI layer which can obscure the deposit
- Lithium reaction products, such as SEI layer
 - Raman and FT-IR: organics/inorganics
 - SEM: SEI layer morphology
 - XPS: SEI layer composition
 - HPLC: identify SEI layer components
- Damage to cathode crystal structure will be elucidated by XRD experiments and morphology changes by SEM observation



SOME FINDINGS FROM FAST-CHARGE EXPERIMENTS

Charging method

CC-CV

30℃







Charge rate

1C

2C

4C

6C

China Fast Charge

25℃





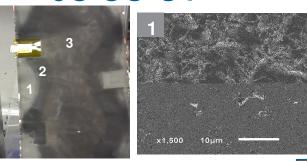


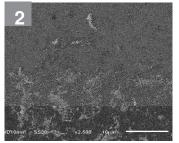


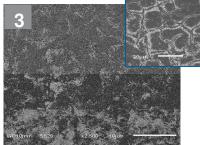


SEM OBSERVATIONS OF FAST-CHARGED ANODES

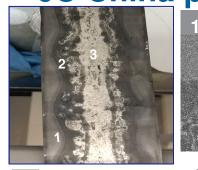
Effect of charging protocol 6C CC-CV

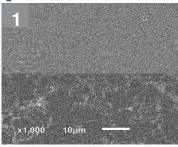


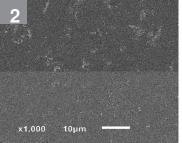


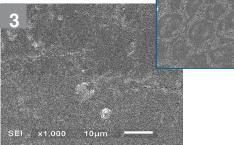


6C China protocol









Microstructures in both protocols are very similar, even though the China protocol laminate has a white/silver streak down the middle.

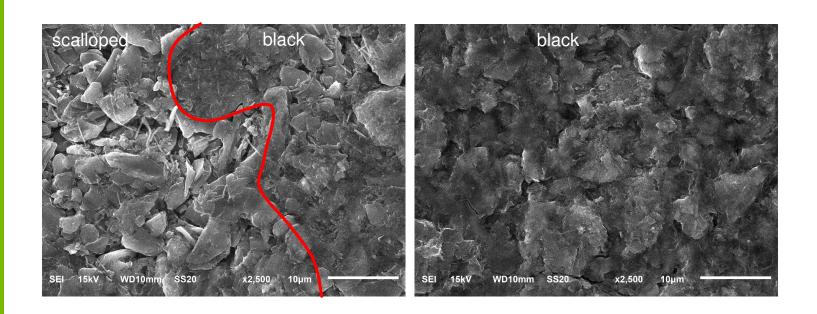
The microstructure in the grey scalloped regions appears unreacted. Trace amounts of V and F are detected throughout each laminate, with the highest concentrations in the central region (area 3). In the central region, some of the graphite particles are covered with a relatively thick crust (image 3 inset) that is cracked and appears amorphous.



TRANSITION AREA DEPENDS ON CHARGING PROTOCOL (1)

6-C, CC-CV

Transition between scalloped and black areas.

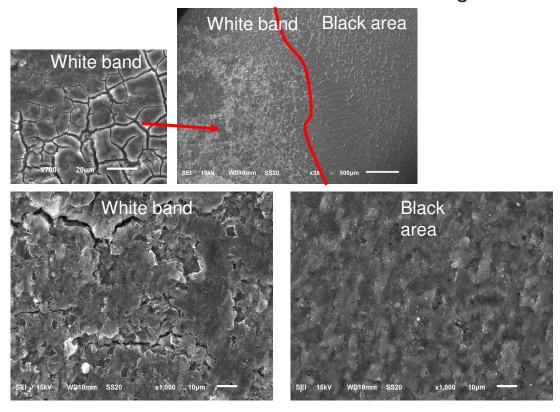


■ In less than 10-20 microns, the transition is complete. All graphite particles are covered.

TRANSITION AREA DEPENDS ON CHARGING PROTOCOL (2)

6-C China protocol

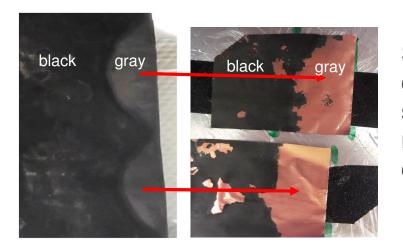
Transition between white band and black region



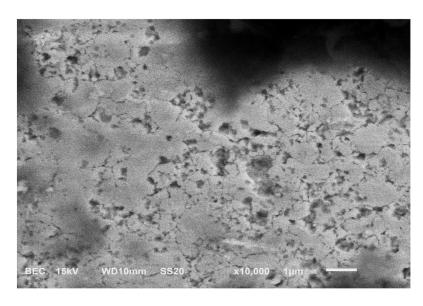
■ The white band is splotchy with some areas covered with a cracked crust.

FAST-CHARGING APPEARS TO IMPACT THE BINDER AND CURRENT COLLECTOR FOIL

CC-CV only at 6-C rate



Stripping the laminate off of the collector with tape shows that the scalloped grey area of the laminate is relatively loosely adhered to the collector.



Evidence of grain boundary etching and pitting corrosion.



SUMMARY AND FUTURE WORK

Summary

- Hardware deliverables from many sources have been tested at Argonne and continue to be evaluated for a variety of vehicle applications
- This testing directly supports DOE and USABC battery development efforts
- The US/China EV testing has shown
 - o Comparing Fast Charge I and III shows results as expected
 - o Faster charge rates accelerate capacity fade and resistance rise
 - o Changes in the anode depend on ambient temperature and rate

Future Work

- Continue to support the DOE and USABC battery development efforts by performing unbiased evaluations of contract deliverables, using standardized test protocols
- Compare results of full fast charge between ANL and CATARC
- Complete collaboration with CATARC using USABC partial charge definitions on LiFePO₄-based cells
- Complete physical characterization of fast-charged cells

Any proposed future work is subject to change based on funding levels



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